

Reactivity of chiral diiminodiphosphine ligands towards $\text{PdCl}_2(\text{PhCN})_2$: synthesis and crystal structures of two unexpected dinuclear palladium(II) complexes

Wai-Kwok Wong,^{a*} Li-Lu Zhang,^a Yang Chen,^a Wai-Yeung Wong,^a Wing-Tak Wong,^b Feng Xue^c and Thomas C. W. Mak^c

^a Department of Chemistry, Hong Kong Baptist University, Waterloo Road, Kowloon Tong, Hong Kong. E-mail: wkwong@hkbu.edu.hk

^b Department of Chemistry, The University of Hong Kong, Pokfulam Road, Hong Kong

^c Department of Chemistry, The Chinese University of Hong Kong, Shatin, N.T., Hong Kong

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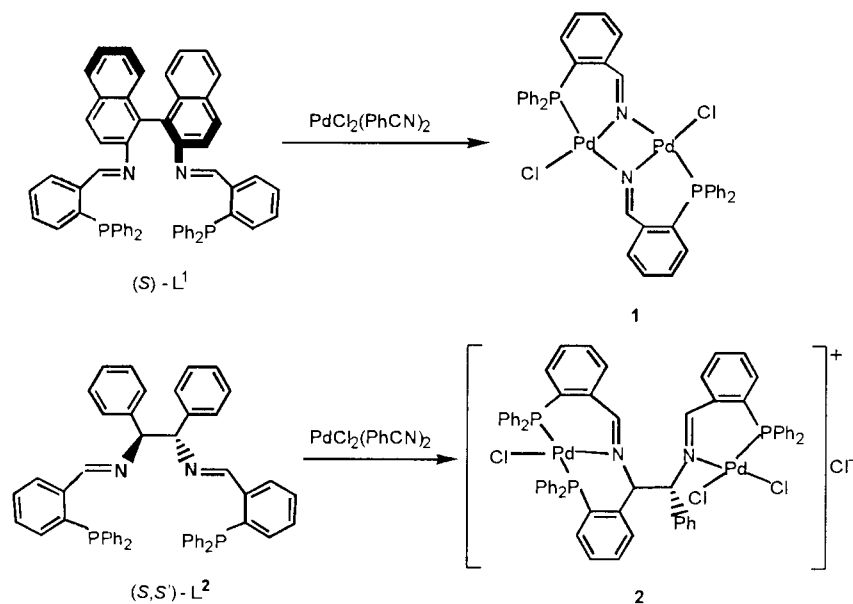
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The interaction of $\text{PdCl}_2(\text{PhCN})_2$ with (*S*)-*N,N'*-bis[2-(diphenylphosphino)benzylidene]-2,2'-diimino-1,1'-binaphthylene (*S*)- L^1 and (*S,S'*)-*N,N'*-bis[2-(diphenylphosphino)benzylidene]-1,2-diimino-1,2-diphenylethane (*S,S'*)- L^2 gave the dimeric complex $\{\text{PdCl}[2-(\text{Ph}_2\text{P})\text{C}_6\text{H}_4\text{CH}=\text{N}]\}_2$ **1** and the dinuclear complex $\{\text{cis-PdCl}_2[2-(\text{Ph}_2\text{P})\text{C}_6\text{H}_4\text{CH}=\text{NCH}(\text{Ph})\text{CH}(\text{C}_6\text{H}_4\text{PPh}_2-2)=\text{NC}_6\text{H}_4(\text{PPh}_2)-2]\text{PdCl}\}\{\text{Cl}\}$ **2**, respectively, whose structures were ascertained by X-ray crystallography.

Transition metal complexes with chiral diamino-, diimino- and diamido-diphosphine ligands have been shown to be effective catalysts for asymmetric hydrogen transfer reactions,¹ epoxidation² and allylic alkylation,³ respectively. Thus, the synthesis of chiral diamino-, diimino- and diamido-diphosphine ligands and their application as auxiliaries for the preparation of chiral catalysts have aroused considerable recent interest. We have investigated the preparation and chemistry of diamino-, diimino- and diamido-diphosphine ligands⁴ and reported the synthesis of *N,N'*-bis[2-(diphenylphosphino)benzylidene]-2,2'-diimino-1,1'-binaphthylene (L^1) and its Cu(I) and Ag(I) complexes.⁵ Here we describe unexpected results of the reactions of $\text{PdCl}_2(\text{PhCN})_2$ with (*S*)- L^1 and (*S,S'*)-*N,N'*-bis[2-(diphenylphosphino)benzylidene]-1,2-diimino-1,2-diphenylethane (*S,S'*)- L^2 (Scheme 1).

Unlike the reactions with Cu(I) and Ag(I), which gave the mononuclear tetrahedral complex $[(\text{Cu}L^1)(\text{BF}_4)]$ or $[(\text{Ag}L^1)$

$(\text{BF}_4)]$,⁵ (*S*)- L^1 reacted with $\text{PdCl}_2(\text{PhCN})_2$ via elimination of the binaphthylene backbone to give the unexpected dimeric species $\{\text{PdCl}[2-(\text{Ph}_2\text{P})\text{C}_6\text{H}_4\text{CH}=\text{N}]\}_2$ **1** in good yield (70%).[†] The structure of compound **1** was established by X-ray crystallography (Fig. 1).[‡] Structural analysis revealed that (*S*)- L^1 has undergone cleavage at the binaphthylene C–N bonds to form two $[2-(\text{Ph}_2\text{P})\text{C}_6\text{H}_4\text{CH}=\text{N}]^-$ units. The dimer is centrosymmetric with the palladium atoms adopting a slightly distorted square planar geometry. The $[2-(\text{Ph}_2\text{P})\text{C}_6\text{H}_4\text{CH}=\text{N}]^-$ moiety behaves as a chelating ligand with P(1) and N(1) coordinated to Pd(1) forming a six-membered ring and as a bridging ligand with N(1) bonded unsymmetrically to two palladium centres. The nitrogen atom acts as a four-electron donor forming a σ -bond with Pd(1) [Pd(1)–N(1), 1.990(5) Å] and a dative bond with Pd(1*) [Pd(1*)–N(1), 2.105(6) Å]. The Pd(1*)–N(1) distance is comparable to the Pd–N distances [2.086(6), 2.164(6) Å] of $(\text{PdL}^3)\text{Cl}_2$ ($L^3 = N,N'$ -bis[2-(diphenylphosphino)benzylidene]-2,2'-diimino-1,1'-biphenylene).⁶ Within the cleaved diimino-phosphino ligand, the N(1)–C(1) distance of 1.236(8) Å is in agreement with the C=N bond distance. The Pd(1), N(1), Pd(1*) and N(1*) atoms form a parallelogram with N(1)–Pd(1)–N(1*) and Pd(1)–N(1)–Pd(1*) angles being 79.9(2) and 100.1(2)°, respectively. The result is in contrast to the reaction of the analogous L^3 ligand with $\text{PdCl}_2(\text{MeCN})_2$, which gives the mononuclear square planar complex $(\text{PdL}^3)\text{Cl}_2$.⁶ This may be due to the fact that the biphenylene backbone is more flexible than the binaphthylene, and can thus accommodate a Pd(II)



Scheme 1

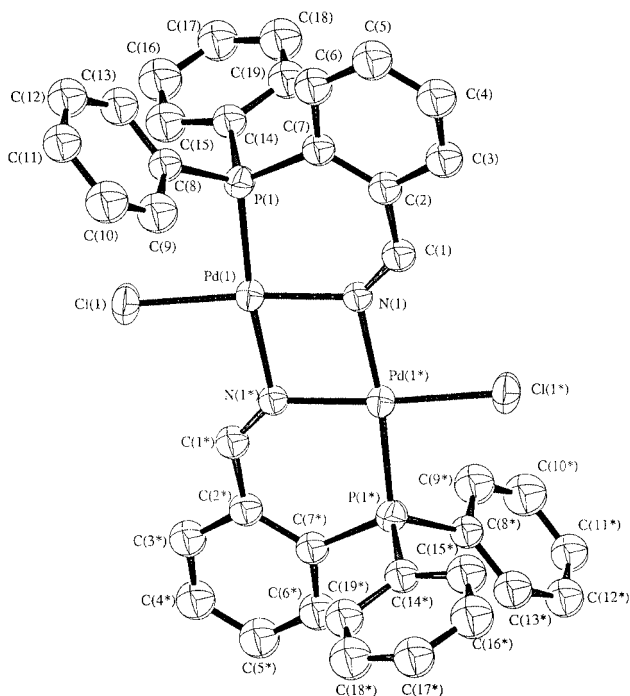


Fig. 1 A perspective drawing of compound **1**. Selected bond lengths (Å) and angles (°): Pd(1)–P(1) 2.217(2), Pd(1)–Cl(1) 2.322(2), Pd(1)–N(1) 1.990(5), Pd(1)–N(1*) 2.105(6), N(1)–C(1) 1.236(8); P(1)–Pd(1)–N(1) 93.7(2), P(1)–Pd(1)–N(1*) 173.1(1), P(1)–Pd(1)–Cl(1) 91.46(7), Cl(1)–Pd(1)–N(1) 174.8(2), Cl(1)–Pd(1)–N(1*) 94.9(2), N(1)–Pd(1)–N(1*) 79.9(2), Pd(1)–N(1)–Pd(1*) 100.1(2), N(1)–C(1)–C(2) 132.1(6).

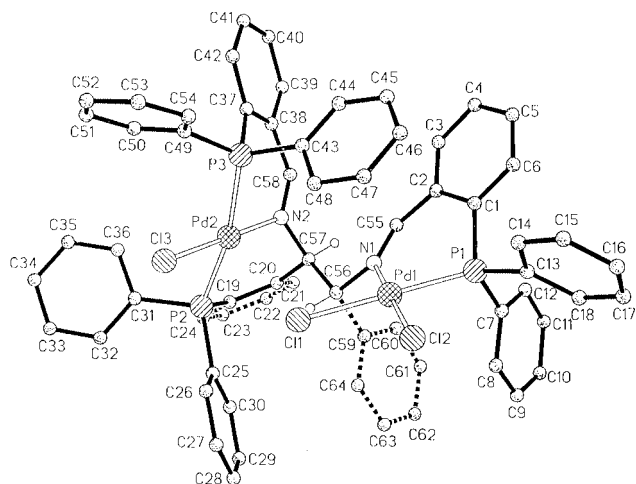


Fig. 2 A perspective drawing of the cation of compound **2**. Selected bond lengths (Å) and angles (°): Pd(1)–P(1) 2.216(2), Pd(1)–N(1) 2.079(4), Pd(1)–Cl(1) 2.346(2), Pd(1)–Cl(2) 2.280(2), Pd(2)–P(2) 2.340(1), Pd(2)–P(3) 2.304(1), Pd(2)–N(2) 2.059(4), Pd(2)–Cl(3) 2.298(2), N(1)–C(55) 1.272(6), N(1)–C(56) 1.528(6), N(2)–C(57) 1.500(6), N(2)–C(58) 1.271(6); N(1)–Pd(1)–P(1), 88.3(1), N(1)–Pd(1)–Cl(1) 92.8(1), N(1)–Pd(1)–Cl(2) 176.0(1), P(1)–Pd(1)–Cl(1) 178.59(5), P(1)–Pd(1)–Cl(2) 90.09(6), Cl(1)–Pd(1)–Cl(2) 88.87(6), N(2)–Pd(2)–Cl(3) 178.8(1), N(2)–Pd(2)–P(2) 91.61(11), N(2)–Pd(2)–P(3) 89.1(1), P(2)–Pd(2)–P(3) 166.68(5), P(2)–Pd(2)–Cl(3) 87.55(6), P(3)–Pd(2)–Cl(3) 91.52(5).

cation to form a square planar complex. These results suggest that the binaphthylene ligand, **L**¹, when behaving as a tetradentate chelating ligand, is sterically more rigid than the corresponding biphenylene ligand and prefers to form a tetrahedral complex.

The interaction of (*S,S'*)-**L**² with PdCl₂(PhCN)₂ in refluxing tetrahydrofuran gave a dinuclear complex {*cis*-PdCl₂[2-(Ph₂P)-C₆H₄CH=NCH(Ph)CH(C₆H₄PPh₂-2)=NC₆H₄(PPh₂-2)]PdCl}·{Cl} **2**,[†] whose structure was established by X-ray crystallography (Fig. 2).[‡] The structure analysis revealed that an *ortho* proton of one of the phenyl rings on the ethane backbone had

been activated and replaced by a diphenylphosphino group. The resulting pentadentate ligand, with two imino and three phosphino donor groups, behaves as a bridging ligand and coordinates unsymmetrically to two different palladium centres in the complex cation. Both palladium atoms adopt a slightly distorted square planar geometry with the Pd(1) atom coordinated to an imino, a phosphino and two chloro groups having a *cis*-PdCl₂ arrangement; and the Pd(2) atom to an imino, a chloro and two phosphino groups having a *trans*-PdP₂ arrangement. The Pd–P [Pd(1)–P(1) 2.216(2), Pd(2)–P(2) 2.340(1), Pd(2)–P(3) 2.304(1) Å] and Pd–N distances [Pd(1)–N(1) 2.079(4), Pd(2)–N(2) 2.059(4) Å] are comparable to those of (PdL³)Cl₂ [Pd–P 2.243(2), 2.262(2); Pd–N 2.086(6), 2.164(6) Å]. The N(1)–C(55) and N(2)–C(58) distances are 1.272(6) and 1.271(6) Å, respectively, and in agreement with the C=N bond distance. The ³¹P NMR data, which are consistent with its solid-state structure show two doublets and a singlet at δ –2.9 (d, *J*_{PP} = 484), 23.1 (d, *J*_{PP} = 484 Hz) and 31.8 (s) for P(1), P(3) and P(2), respectively.

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Notes and references

[†] Synthetic procedures for compound **1**: A solution of (*S*)-**L**¹ (0.08 g, 0.1 mmol) in tetrahydrofuran was added dropwise to a solution of PdCl₂(PhCN)₂ (0.04 g, 0.1 mmol) in tetrahydrofuran (25 cm³) at room temperature over a period of 15 minutes, during which a yellow precipitate was obtained. After stirring at room temperature for an additional 5 h, the precipitate was filtered, washed with diethyl ether (2 × 20 cm³) and recrystallized from a chloroform–diethyl ether solution to give pale yellow crystals, which were filtered and dried *in vacuo*. Yield: 0.04 g, 70%; mp 221–222 °C. NMR (CDCl₃): ³¹P, δ 27.5 (s); ¹H, δ 8.88 (d, 2H, *J*_{PH} = 9.7 Hz, –N=CH–), 6.80–7.75 (m, 28H, phenyl). IR (in KBr): ν_{C=N}, 1621 cm^{–1}. Found (calc. for C₃₈H₃₀Pd₂Cl₂N₂P₂·2CHCl₃): C, 43.3 (43.7); H, 2.9 (2.9); N, 2.3 (2.6)%.

For compound **2**: A solution of (*S,S'*)-**L**² (0.11 g, 0.14 mmol) and PdCl₂(PhCN)₂ (0.05 g, 0.14 mmol) in tetrahydrofuran (25 cm³) was refluxed for 8 h to give a yellow precipitate. The precipitate was filtered, washed with tetrahydrofuran and recrystallized from a mixture of DMF–methanol–diethyl ether to give yellow crystals, which were filtered and dried *in vacuo*. Yield: 0.07 g, 35%; mp 211–214 °C. ³¹P NMR (CDCl₃): δ –2.9 (d, *J*_{PP} = 484), 23.1 (d, *J*_{PP} = 484 Hz), 31.8 (s). IR (in KBr): ν_{C=N}, 1668vs, 1630s cm^{–1}. MS (FAB, +ve) *m/z*: 1257 [(M – 2Cl) for ¹⁰⁶Pd and ³⁵Cl]. Found (calc. for C₆₄H₅₁Pd₂Cl₄N₂P₃·C₃H₇NO·2CH₃OH): C, 57.5 (57.9); H, 4.8 (4.6); N, 3.0 (2.9)%.

[‡] Crystal data for **1**: C₃₈H₃₀Pd₂Cl₂N₂P₂, yellow plate, 0.03 × 0.24 × 0.25 mm, *M* = 860.32, monoclinic, *P*2₁/*n* (no. 14), *a* = 9.889(1), *b* = 17.607(2), *c* = 10.282(1) Å, β = 107.90(1)°, *V* = 1703.6(3) Å³, *Z* = 2, *T* = 298 K, μ(Mo–K_α) = 13.38 cm^{–1}, 16020 reflections measured, 2685 unique, final *R* = 0.047, *R*_w = 0.036 (based on *F*) for 1755 [*I* > 1.5σ(*I*)] observed reflections. For **2**·CH₃OH: C₆₄H₅₁Pd₂Cl₄N₂P₃·CH₃OH, yellow prism, 0.16 × 0.16 × 0.40 mm, *M* = 1327.62, triclinic, *P*1 (no. 2), *a* = 12.574(1), *b* = 13.636(1), *c* = 20.058(1) Å, α = 80.03(1), β = 75.67(1), γ = 81.04(1)°, *V* = 3258.8(4) Å³, *Z* = 2, *T* = 293 K, μ(Mo–K_α) = 8.29 cm^{–1}, 9163 reflections measured, final *R*₁ = 0.061 for 7937 [*I* > 2.0σ(*I*)] observed reflections, *wR*₂ = 0.164 (based on *F*²) for 9163 unique reflections. CCDC reference number 186/1913. See <http://www.rsc.org/suppdata/dt/b0/b001245i/> for crystallographic files in .cif format.

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